Mayne et al.

4,217,142 * Aug. 12, 1980 [45]

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[54]	METAL CO	DATING COMPOSITIONS	[58] Field	of Search	106/14.23, 14.28, 14.36, 21/2.7 R; 252/389 R, 39; 427/156,
[75]	Inventors:	John E. O. Mayne, Cambridge; Peter		100/ 245,	327
		J. Heyes, Barnsley, both of England	[56]	R	leferences Cited
[73]	Assignee:	National Research Development		U.S. PA	TENT DOCUMENTS
		Corporation, London, England	2,671,758	3/1954	Vinograd
[*]	Notice:	The portion of the term of this patent subsequent to Jan. 23, 1996, has been disclaimed.	2,726,215 3,028,247 3,035,005	12/1955 4/1962 5/1962	Jones
			•		Hosea E. Taylor
[21]	Appl. No.:	907,015			-Amelia B. Yarbrough <i>irm</i> —Oblon, Fisher, Spivak,
[22]	Filed:	May 17, 1978	McClelland	•	
			[57]		ABSTRACT
	Rela	ted U.S. Application Data	The use of	magnesiu	m azelate as a new rusting inhibitor
[63]	Continuatio	n of Ser. No. 714,397, Aug. 16, 1978.	-		cribed. The preferred inhibitor is a
[30]	Foreig	n Application Priority Data		_	im azelate and a basic oxide e.g. the proportion of 3:1 to 10:1 by
Aug	g. 29, 1975 [G	B] United Kingdom 35718/75	weight. Th	ne new fo	rmulations are substitutes for lead nate primers and confer excellent
[51]			protection	on iron a	nd steel.
[52]	U.S. Cl	106/14.36; 106/243; 252/389 R		12 C	laims, No Drawings

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METAL COATING COMPOSITIONS

This is a continuation, of application Ser. No. 714,397 filed Aug. 16, 1978.

This invention relates to protective coatings and more particularly to coating compositions for the protection of metal surfaces.

The invention will be introduced with reference to the protection of iron and steel against corrosion, but it 10 has broader application to other metallic substrates as will appear hereinafter. The rusting of iron is a very well understood process and the protection of this metal against rusting by the application of coating compositions containing red lead has a long history. Red lead 15 pigment in a conventional drying oil vehicle is well known to confer excellent protection by a mechanism involving degradation of compounds formed between the lead oxide and the fatty acid components of the drying oil. These compounds, the lead soaps, degrade in 20 the presence of water and oxygen to yield a variety of compounds which are inhibitive, the most important being lead azelate. Lead azelate is continually formed by the breaking down of unsaturated fatty acids present in, for example, the linseed oil vehicle and the resulting 25 lead azelate and other compounds inhibit rust formation by blocking weaknesses in the naturally occurring oxide film on the iron surface.

The knowledge of the protective mechanism described above has prompted proposals to use various 30 azelates as pigments. Surprisingly, however, when lead azelate, calcium azelate and zinc azelate are formulated in inert vehicles (different from the conventional drying oils), results have been largely unsuccessful.

It has now been found that magnesium azelate has 35 excellent inhibitive properties and the present invention, therefore comprises a protective coating composition containing inhibitive amounts of magnesium azelate.

The amount of magnesium azelate in the coating 40 composition required to produce an acceptable level of inhibition may be readily detected by experiments with the particular metal for which protection is required. For example, for the protection of iron and steel coating compositions calculated to deposit from about 1% to 45 about 10% by weight of magnesium azelate based on the weight of the dry film are highly effective. In practice proportions of at least 2% by weight and preferably from about 4% to about 6% by weight are recommended. Conveniently the composition may be in the 50 form of a base preparation requiring dilution as appropriate at the time of use.

Preferably magnesium azelate is used in conjunction with a basic metal oxide e.g. an alkaline earth metal oxide which acts to raise the pH of the environment 55 between the dried coating and the underlying metal which is created when water penetrates through the protective layer. Magnesium oxide is a good example of such an added material. Combinations of magnesium azelate and magnesium oxide in the proportions of from 60 about 3:1 to about 10:1 give excellent results.

The coating compositions of the present invention may be oil-based or water-based. Thus, the inhibitor may be present in conventional drying oils or any of the more recently developed synthetic film-forming poly- 65 C. mers and copolymers which are now in current use in paint technology. Magnesium azelate may also be used in the so-called emulsion paints which are aqueous po

emulsions or colloidal solutions of drying oils, modified drying oils, or suitable polymeric compositions, or any mixture thereof; with these the inhibitor is present in solution and may also be present in suspension. Particularly in the oil-based paints, magnesium azelate confers the additional advantages of body and structure and ready dispersibility on the composition.

The invention is of especial importance in protective coating compositions which are lead free, the use of lead bearing compositions being at present in disfavour except under closely controlled conditions. Various chromates e.g. zinc chromate are currently available as alternatives to red lead (although they function by a different mechanism), but these are also subject to criticism and the present invention has particular application to compositions which are also free of such chromates.

The present invention also includes a process for the protection of a metal surface which comprises applying to the surface a coating containing magnesium azelate.

The invention may be used for the protection of a variety of metals and alloys including iron and steel, dural, aluminium, zinc and others. The compositions of the invention are essentially priming paints for metal surfaces and preferably require the subsequent application of adherent layers of highly impermeable filmforming materials. However, they are very persistent on, and effective on, surfaces which remain non-top-coated for some considerable time which, in view of the relatively high water-solubility of magnesium azelate, is remarkable. Results obtained so far for the protection of mild steel indicate a high level of inhibition comparable with that obtained with red lead and at least as good as that obtained with zinc chromate and zinc phosphate.

Typical coating compositions in accordance with the invention are described in the following Examples in which all parts are given by weight.

In the Examples, the following film forming compositions were employed:

Beckalide 5065 is a 65% solution of a polyamide resin having an amine number of about 140 to 150; and acid value of less than 7; and a specific gravity of 0.924 in a xylene-isopropanol mixture.

Beckurane 79-60 is a polyurethane oil having a Gardner viscosity of z-z₂; a Gardner color of 6; an acid number of less than 0.5; a specific gravity of 0.960; a free NCO content of 0.0%, which is the reaction product of diiocyanate with a material having a reactive hydrogen atom.

Epikote 1001 is an epoxide resin which melts at from 64°-76° C.; has a viscosity of 0.8 to 1.7 poises at 25° C.; an epoxide equivalent of from about 450-525; an equivalent weight of 130; and an average molecular weight of 900.

Styrenated Alkyd Scopol 51 NX is a styrene modified alkyd having a styrene content of approximately 16%; a phthalic acid content of approximately 30.5%; and 46% of mixed, non-yellowing fatty acid oils which have been esterified with glycerol and xylene as the solvent. The total non-volatile content is about 70, $\pm 1\%$.

Versamid 115 is a reactive polyamide resin with a conventional coating curing agent having a maximum acid value of 4, and a viscosity of 500-600 poises at 40° C

Vinacryl 7175 is an anti-corrosive metal primer which is an aqueous emulsion of a styrene-acrylic copolymer, having a non-volatile content of 50%, a vis-

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cosity of 0.2 to 0.5 poises at 25° C., a pH of from 6.5 to 7.0, containing an anionic emulsifier.

EXAMPLE 1

Vinacryl 7175 Styrene-acrylate	
aqueous emulsion (50% solids)	849
TiO ₂	40.7
Magnesium azelate	42.2
Suspending agent (Modocoll E600)	0.6
Dispersing agent (Calgon S)	1.2
880 Ammonia	12
Preservative	0.4
Water	46

The above composition has been applied to mild steel 15 test panels in an industrial exposure site in South London. After 18 months the condition of the paint film is still excellent even though not top coated. The test panels compare favourably with control panels treated 20 with emulsion based zinc chromate.

EXAMPLE 2

Polyurethane alkyd oil (Beckurane 79-60)	85
Cobalt naphthenate (6% cobalt in white spirit)	0.4
Magnesium azelate	15
Solvent (White Spirit)	50

EXAMPLE 3

Polyurethane alkyd oil (Beckurane 79-60)	85
Cobalt naphthenate (6% cobalt in white spirit)	0.4
Magnesium azelate	12
Magnesium oxide	3
White Spirit	50

EXAMPLE 4

Polyurethane alkyd oil (Beckurane 79-60)	85
Cobalt naphthenate (6% cobalt in white spirit)	0.4
Magnesium azelate	13.5
Magnesium oxide	1.5
White Spirit	50

EXAMPLE 5

Epikote 1001 (70% solution in xylene-	
butanol 3:1)	49
Beckalide 5065 (65% solution in xylene-	
butanol 3:1)	36
Magnesium azelate	15
Xylene	30
Butanoi	10

FYAMPLE 6

Epikote 1001 (70% solution in	
xylene-butanol 3:1)	49
Beckelide 5065 (65% solution in	
xylene butanol 3:1)	36
Magnesium azelate	13.5
Magnesium oxide	1.5
Xylene	30
Butanol	10

EXAMPLE 7

Primer formulations are made up as follows including a standard zinc chromate primer and primers A and B 5 according to the invention. Figures represent grams weight.

		TABLE		
		Control	Primer A	Primer B
10	Red Iron Oxide ED9	47.25	47.25	47.25
••	Zinc Potassium Chromate	10.12		
	Magnesium Azelate		4.23	6.35
	Magnesium Oxide	_	1.06	1.60
	Celite 281	6.75	6.75	3.30
	China Clay	3.37	3.37	3.38
15	Styrenated Alkyd Scopol			
1.5	51NX (70% solids)	37.70	37.70	37.70
	Calcium Naphthenate 5%	1.30	1.30	1.30
	Cobalt Naphthenate 5%	0.2	0.22	0.22
	MEK Oxime	0.20	0.26	0.26
	Xylene	as required	as required	as required
20	PVC	39%	39%	39%
20	Active pigment	7.02% by	7.02% by	10.5% by
		volume on solids	volume on solids	volume on solids
		10.8% by	6.0% by	9.07% by

The above panels have been subjected to conventional tests including

weight

weight

weight

- (1) salt spray (REL cabinet 3% sodium chloride solution)
- (2) sulphur dioxide/humidity (British Standard 3900 Part F8)
- (3) humidity cabinet (British Standard 3900 Part F2). After 250 hours exposure in the salt spray test the control panels show general low intensity rust spotting 35 whereas with primer A few rust stains appear and with primer B there is a greatly reduced intensity of attack. In the sulphur dioxide/humidity test the control panels after 7 cycles are in poor condition with moderate to severe rust spotting and streaking. Panels treated with 40 primer A show very light spotting confined to the panel edges. The primer B panels are in good condition. In the humidity cabinet test after 1000 hours panels treated with primers A and B are clearly in superior condition to those in the control. The primer B panels are in par-45 ticularly good condition throughout.

EXAMPLE 8

Primer formulations are made up as follows including a standard strontium chromate primer and primers C and D according to the invention. Figures represent grams weight.

TA	BL	E
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TABLE				
	Control	Primer C	Primer D	
Titanium Dioxide	21.5	21.5	21.5	
Anatase E				
Micronised	54.0	54.0	34.5	
Asbestine				
Celite 281	33.0	33.0	21.5	
Strontium Chromate	85.5			
Magnesium azelate		36.0	54.0	
Magnesium oxide		4.0	6.0	
Epikote 1001	40% solution	40% solution	40% solution	
•	211.0	211.0	211.0	
Thinners	(1/1/1 by weight and methyl eth	ght xylene, n but lyl ketone)	tyl alcohol	
	as required	as required	as required	
Activator	30% solution	30% solution	30% solution	
Versamid 115				
Mixing ratio	100 base/	100 base/	100 base/	
	33.4 acti-	39.2 acti-	40.4 acti-	

TABLE-continued

	Control	Primer C	Primer D
PVC	vator. 34.9%	vator. 34.9%	vator. 34.97%
Active pigment	13.2% by volume on solids 26.7% by weight on solids	13.2% by volume on solids 14.6% by weight	19.8% by volume on solids 22.7% by weight

Magnesium azelate may also be used in other ways to protect metals against corrosion e.g. as an additive in water systems of various kinds.

We claim:

- 1. In a protective coating composition which protects metal surfaces against corrosion and comprises a film forming vehicle and corrosion inhibitor, the improveinhibitor in an effective amount.
- 2. The protective coating composition of claim 1, wherein the quantity of magnesium azelate in said composition is sufficient to provide a dry film containing at 25 least 1 wt.% magnesium azelate.
- 3. The protective coating composition of claim 1 in which the proportion of magnesium azelate is such as to deposit from about 1% to about 10% by weight of the dry film.

- 4. The protective coating composition of claim 3 in which the proportion of magnesium azelate is such as to deposit from 4 to 6% by weight.
- 5. The protective coating composition of claim 2 5 wherein an alkaline earth metal oxide is present.
 - 6. The protective coating composition of claim 5 wherein the alkaline earth metal oxide is magnesium oxide.
- 7. The protective coating composition of claim 5 10 wherein the proportion of magnesium azelate to alkaline earth metal oxide is in the range from 3:1 to 10:1 by weight.
- 8. The protective coating composition of claim 7 in which the proportion of magnesium azelate to alkaline 15 earth metal oxide is about 4:1.
 - 9. The protective coating composition of claim 1 which is free of lead.
- 10. In a method for protecting a metal surface from corrosion by applying to said surface an adherent coatment comprising magnesium azelate as said corrosion 20 ing composition containing a film forming vehicle and an effective amount of a corrosion inhibitor, the improvement comprising magnesium azelate as said corrosion inhibitor.
 - 11. The method of claim 10, wherein said coating composition contains sufficient magnesium azelate to provide a dried film containing at least 1 wt.% magnesium azelate.
 - 12. The process of claim 10 wherein the metal is iron or steel.

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UNITED STATES PATENT AND TRADEMARK OFFICE CERTIFICATE OF CORRECTION

PATENT NO.: 4,217,142

DATED : Aug. 12, 1980

INVENTOR(S): JOHN E.O. MAYNE ET AL

It is certified that error appears in the above—identified patent and that said Letters Patent are hereby corrected as shown below:

Related U.S. Application Data

Continuation of Ser. No. 714,397, Aug. 16, 1976. [63]

Bigned and Sealed this

Twenty-eighth Day of October 1980

[SEAL]

Attest:

SIDNEY A. DIAMOND

Attesting Officer

Commissioner of Patents and Trademarks